TITLE: Creation of a nanovascular network by electrospun sacrificial nanofibers for self-healing applications and its effect on the flexural properties of the bulk material.

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ABSTRACT:

Composites, increasingly significant due to their excellent properties, are prone to failure over time. Self-healing materials are being developed to extend their lifetime. Despite continuous progress, the effect of introducing such healing feature on the mechanical properties of the neat material is mainly overlooked. Therefore, we created a nanocomposite and a nanovascular network by pullulan sacrificial nanofibers, and analysed the flexural properties in comparison to the neat matrix. A parameter analysis of the electrospinning process allowed producing tailored pullulan nanofibers. Their introduction showed no effect on the strength and modulus of the epoxy matrix. On removal of the pullulan nanofibers, the properties of the resultant nanovascularized epoxy were somewhat reduced relative to the neat epoxy depending on volume fraction and diameter of the nanochannels. Interestingly, the decrease of mechanical properties of the nanovascular epoxy is lower than by introducing microcapsules,

and opens potential for a more appropriate introduction of self-healing systems in polymeric matrices.

KEYWORDS: Self-healing; vascular network; electrospinning; sacrificial pullulan nanofibers; humidity; flexural properties

1. INTRODUCTION

As materials get damaged during use, regular maintenance checks are needed and components may need to be replaced. To increase the durability and reliability of materials, self-healing strategies are being looked at. Extrinsic healing agents are pre-embedded in microcapsules, hollow fibers or in a vascular network within the material and, after damage is induced (locally), the healing agents will be released and will react autonomously, healing the crack generated in the material before it can result in complete failure of the component [1].

In contrast to capsule-based healing, vascular self-healing systems are being developed to permit repeated healing at a given location and to enable self-healing agents to reach more distant points of the substrate. Self-healing vascular systems reported so far have channel diameters from 20 µm to even millimetre size, with the vast majority having diameters of hundreds of micrometres [2–5]. Electrospinning allows for the large-scale production of submicron fibers which, after embedding in a matrix and selective dissolving, will result in a vascular network of channels with diameters that can be decreased to a few hundreds of nanometers. As such, electrospinning was introduced for creating nanofluidic channels in a polymeric matrix [6]. Some first studies on sacrificial polyethylene oxide as well as sugar structures, such as pullulan, have been shown to allow the creation of a nanovascular network in a polydimethylsiloxane matrix as well as an epoxy matrix [6–8].

Although important progress has been made on self-healing systems, the possibly negative impact on the mechanical properties of the neat polymer matrix due to the introduction of artefacts created by microcapsules or a microvascular system is little studied. To the best of our knowledge, a mechanical study of the effect of introducing a nanovascular network has not been reported yet. Also, for microcapsule-based systems, that have been the most favoured technology in self-healing applications for composite materials so far, this is often overlooked. The few studies available conclude that the addition of microcapsules to an epoxy matrix significantly decrease the tensile modulus and ultimate strength of the neat epoxy matrix [9–12]. Further, the introduction of a microvascular network or even hollow glass fibers (HGF) in fiber-reinforced composites is reported to distort the reinforcement architecture due to the large reservoirs [13–15]. However, introducing such 'defects' in a material designed for its excellent mechanical properties, will only be done if these properties do not drop drastically. Introducing a nanostructured network that does not deform the reinforcement and creates fewer or smaller artefacts in the epoxy matrix may very well solve these problems.

The present paper aims to study the impact of introducing a nanovascular system on the mechanical properties of the neat matrix material. It provides insight into the creation of nanocomposites (with solid pullulan nanofibers) and nanovascular networks (with empty nanochannels), and the effect they both have on the mechanical properties of the resulting nanocomposite or nanovascularized epoxy matrix. The tests performed on epoxy samples with empty nanovascular networks are expected to be representative for the properties of self-healing epoxy matrices with a nanovascular network containing low viscosity liquid healing agents, which would have negligible mechanical properties. The comparison of both the epoxy containing the pullulan nanofibers and the epoxy having a nanovascular network to the neat epoxy material is also of relevance for the future use of coaxial nanofibers in

nanostructured self-healing composite materials, as the effect of these core-shell nanofibers, containing the liquid healing agent inside a solid polymer shell, is expected to lie between these two extremes. The methodology involves the production and testing of nanocomposites (with solid pullulan nanofibers) and the nanovascular network (with empty nanochannels), as illustrated in Figure 1. To create a network of sacrificial nanofibers, pullulan, a water-soluble natural polysaccharide, was chosen for electrospinning. This allows for an environment-friendly process, as the use of harmful organic solvents is avoided. An optimised electrospinning process of pullulan nanofibers aims to allow for targeted nanovascular networks with optimal channel spacing and a range of diameters. Vacuum-assisted resin transfer moulding (VARTM) was used to embed the sacrificial nanofibers in a relatively big epoxy plate (30 x 30 cm). After curing the epoxy, the nanofibers were selectively dissolved, creating a nanovascular network inside the epoxy matrix. To assess the potential of nanovascular systems for self-healing applications, flexural tests were performed on bulk epoxy samples loaded with different volume fractions of nanofibers or nanochannels and for different diameters.

FIGURE 1

2. MATERIALS

Food-grade pullulan with a molar mass of 200 kDa and a density of 1.85 g/cm^3 was kindly provided by Hayashibara Biochemical Laboratories Inc. The epoxy resin was composed of EPIKOTE resin MGS RIMR135 (with a density of 1.15 ± 0.02 g/cm^3) and EPIKURE curing agent MGS RIMH137 (with a density of 0.96 ± 0.03 g/cm^3), both from Hexion in a 100:30

weight ratio. This is a state-of-the-art infusion resin designed for windmill applications that has a low viscosity and a high fracture toughness.

3. EXPERIMENTAL

For electrospinning, all the solutions were freshly prepared with deionised water in order not to have biological degradation. A climatized mononozzle setup was used to study the concentration and humidity window for stable electrospinning, and a multinozzle setup was used to electrospin the targeted nanofibrous membranes at upscaled dimensions for the fabrication of the composites. In both cases, the polymer solutions were pumped with a flow rate of 1 mL/h through a nozzle with an inner diameter of 1.024 mm. The tip to collector distance was 20 cm and the voltage was varied between 15 and 30 kV until a stable electrospinning process was achieved. The setup is composed of a voltage source (Glassman High Voltage Series EH30P3), an infusion pump (KD Scientific Syringe Pump Series 100), and a grounded collector plate, and is operated in a climate chamber (Weiss WK 340/40) for the mononozle setup. For the concentration study, all solutions (10-40 wt%) were electrospun at 23 ± 1.5 ºC and 50 ± 3 % relative humidity (RH). For the humidity study, the solutions (15-35 wt%) were electrospun at a temperature of 23 ± 1.5 ºC, and the relative humidity was varied from 30 % to 70 % ± 3 % RH. The large nanofibrous membranes were electrospun at 23 ± 2 ºC and 50 ± 10 % RH.

The nanocomposites were produced by VARTM using an aluminium mould of 40 cm x 40 cm x 3 mm. The epoxy was cured according to the manufacturer-recommended curing cycle (24 h at RT, followed by a postcure at 80 ºC for 15 h). To achieve an epoxy with an (empty) nanovascular network, the pullulan nanofibers were dissolved by immersion of the flexural-test specimens (see dimensions below) in stirred water during one (for 830 nm

nanofibers) to four weeks (for 230 nm nanofibers). Neat epoxy control specimens to be compared with the nanovascularized epoxy also underwent these treatments.

Scanning electron microscopy (SEM, Jeol Quanta 200F FE-SEM) was used to investigate the diameter and morphology of the electrospun nanofibers. The nanofiber diameter was measured with ImageJ software by taking an average of 50 measurements on at least 5 different images of the membrane. Prior to the SEM measurements, the specimens were coated by a gold sputter coater (Balzers Union SCD 030).

The viscosity of the solutions was measured at 20 ºC with an AR-G2 rheometer using a steel plate and a cone of 40 mm and 2 º. The shear rate was varied from 0.1 to 10 s^{-1}; depending on the concentration of the aqueous solution.

The flexural tests were performed on an electromechanical Instron 5800R machine following ASTM D 790 (comparable to ISO 178:2010). At least five specimens were tested per sample. The specimens were loaded on a three-point-bending setup using a span length of 48 mm. The beam size was 60.4 mm x 12.7 mm x 3 mm. The strain rate was 0.10 min^{-1}. According to the ASTM norm, the strength is taken as the maximum flexural stress during the bending test up to 5.0 % strain and the flexural modulus is calculated taking the slope from 0.5 to 0.9 % strain in the stress-strain curve.

4. RESULTS AND DISCUSSION

4.1. Nanofiber production

Nanovascular network properties, such as the flow of the healing agents and the deterioration of mechanical properties, are determined by the size of the nanochannels. To target specific nanovascular networks, the nanofiber diameter and morphology are crucial factors, which can be tuned through adjusting the electrospinning parameters. Concentration, polymer molar

mass and humidity are the major electrospinning parameters that affect fibre diameter [16–20].

The concentration of the solution has a large influence on the electrospinning process, as it determines the viscosity of the solution, which is related to the entanglement of the polymer chains in the solution [21]. The viscosity of the aqueous pullulan solutions was found to increase according to a power law with the concentration (Figure 2). To screen the potential for the production of nanovascular networks, aqueous pullulan solutions of concentrations ranging from 10 to 40 wt% were electrospun during 15 minutes under stable conditions. SEM images of the electrospun nonwovens reveal that the morphology changes from beads and beaded nanofibers (for solutions of 10 and 15 wt%) to defect-free nanofibers (20-30 wt%) and even branched or interconnected nanofibers (for 35 and 40 wt%). At the same time, the nanofiber diameter increases linearly with the polymer concentration from below 100 nm (10 wt%) to more than micrometer size (Figure 2). For the highest concentrations (35 and 40 wt%), the nanofiber diameter distribution is broader due to the presence of branched or interconnected fibers. This can be explained by the lower concentration of solvent in these samples, which quickly evaporates altering the shape and charge per unit area of the jet and thus creating instabilities. These can be overcome by secondary jets that emerge from the primary jet, creating branched nanofibers and interconnections between nanofibers [22]. To have minimum entanglement of the polymer chains, thus preventing the jet from breaking, and getting defect-free nanofibers, the concentration should be around 20 wt%.

FIGURE 2

As water is used as solvent for the electrospinning, the humidity in the electrospinning environment also has a big effect on the morphology and diameter of the pullulan nanofibers produced. At a given temperature, the evaporation rate of water increases as the humidity decreases [23]. If the water evaporates faster, the electrospinning jet will solidify earlier, leading to thicker nanofibers. On the other hand, if the relative humidity is high, the evaporation rate of water will decrease, and the jet will have more time to elongate the fiber before the solvent is evaporated and, consequently, thinner nanofibers will be produced. Besides the effect of the evaporation rate of water, the plasticizing effect of water on pullulan will also play a role in the further stretching of the nanofiber [24]. At too high humidity, beads may be formed, especially for low pullulan concentrations, because, as the evaporation rate decreases, the viscosity remains lower for a longer time and capillary breakup of the spinning jet occurs, leading to beaded nanofibers [19,25]. The SEM images of pullulan nanofibers electrospun at different humidities and concentrations are shown in Figure 3.

FIGURE 3

Figure 3 shows that only in the case of 25 wt% are defect-free nanofibers produced at any humidity. For 15 wt% solutions, defect-free nanofibers were electrospun only at 30 % RH; beaded nanofibers were electrospun at higher humidity with a higher concentration of beads and a shorter spacing between them at 70 % RH. For the highest concentration, 35 wt%, branched fibers were obtained at lower humidity, while defect-free nanofibers are created as the humidity is increased.

In addition to changes in fibre and network morphology, the diameter of the pullulan nanofibers decreases linearly with increasing humidity (Figure 4). When branched nanofibers

are created at lower humidities, the distribution of diameters is broader (as indicated by the error bars in Figure 4) and the amount of interconnections between the nanofibers increases. While branched nanofibers may be advantageous for future nanovascular applications, we are at present interested in the more homogeneous distribution. Therefore, solutions of 20 and 25 wt% pullulan electrospun under 50 % RH were chosen for the preparation of the nanocomposites in the next section.

FIGURE 4

4.2. Nanocomposite and nanovascular network fabrication

The pullulan nanofiber networks electrospun with the conditions chosen in the previous section were used to create epoxy samples containing a nanovascular network, as illustrated in Figure 5. First, the electrospun nanofibers (Figure 5a) are embedded in an epoxy resin. Curing the epoxy results in a nanocomposite (Figure 5b),that will be used to test the influence of embedding solid pullulan nanofibers on the properties of the epoxy matrix. The creation of a nanovascular network was accomplished by selectively dissolving the embedded pullulan nanofibers in a stirred water bath (Figure 5c). These samples were used to study the influence of introducing a nanovascular network in the epoxy matrix.

FIGURE 5

The dissolution of the nanofibers was performed by immersion of the specimens in stirred water, for the samples with coarser nanofiber diameter (C6-coarse and C9-coarse), it took 12

to 15 days to complete the dissolution process and for samples with finer nanofibers (C6-fine and C9-fine) it was approximately one month. The dissolution was tracked by weight change of the specimens (Figure 6); in addition they changed from translucent to opaque when completely dissolved. An interconnected network was formed, as it can be seen in Figure 5c. Where the nanochannels which are crossing meet, there is an interconnection (shown inside the circle in Figure 5c). Other nanochannels which are in the same direction converge at one point, as shown by the three nanochannels in the square of Figure 5c. Furthermore, this was also proven by immersing just the bottom of a specimen in dyed water; after few days, the dyed water reached the top of the specimen by capillary flow.

FIGURE 6

4.3. Mechanical testing

Flexural tests were performed on the nanocomposite and the nanovascular network, as well as on neat epoxy control specimen (E). The latter were fabricated and processed in the same way as the nanocomposites (but without any electrospun nanofibers inside) to avoid any influence of hygrothermal effects. The flexural results of the pullulan-epoxy nanocomposites (as in Figure 5b), are shown in Table 1. There is no reduction in flexural strength or modulus, for neither the finer nor coarser pullulan nanofibers. Also, increasing the volume fraction of nanofibers from 6 to 9 vol% does not influence the properties of the matrix.

Table 1: Volume fraction of pullulan nanofibers, average fiber diameter, flexural strength (σ) and modulus (E) of the samples tested. Sample designation: E stands for neat epoxy control; F stands for nanocomposites and the volume percentage and size of the nanofibers are indicated by the number and the last word, respectively).

Sample	Nanofibers (vol %)	Diameter (nm)	σ (MPa)	E (GPa)
E	0	-	115 ± 4 [a]	3.0 ± 0.2 [b]

F6-fine	6	390 ± 83	113 ± 11	3.0 ± 0.3
F6-coarse	6	760 ± 92	117 ± 6	3.1 ± 0.1
F9-fine	9	250 ± 65	111 ± 13	3.4 ± 0.1

[a, b]: These results are in accordance with the manufacturer's specifications [26].

Table 2 summarizes the flexural strength and modulus of the nanovascularized epoxy samples (as in Figure 5c). The flexural strength decreases with the introduction of the nanochannels in the material, as is expected for a porous sample. Besides this effect, we observed that there might be some water uptake by the epoxy matrix during the immersion in water as the strength of the virgin epoxy decreases from 115 (for the neat epoxy control, E) to 104 MPa (for the water immersed epoxy control, E-H_2O). For the nanovascularized epoxy, this effect might be maximized as there is more contact surface with the water. Comparing the nanovascularized epoxy samples to the water immersed epoxy control (E-H_2O), the reduction in strength is lower for the two nanovascular samples with lowest volume fraction of open nanochannels, and the finer nanochannels result in a smaller strength reduction. This is true for both the C6 and C9 samples. This is important to note because, even although the difference in size is not large (<500 nm), the strength reduction is significantly lower in the case of smaller nanochannels. Thus, although a reduction of mechanical properties cannot be neglected with the introduction of a porous network in the epoxy matrix, it is clear that using a finer distributed network will be less detrimental. In addition, the results given here show a worst case scenario, as they report the properties of bulk epoxy matrix. If applied to a composite, the introduction of the reinforcing fibers will reduce the negative effect of the nanovascular system on the mechanical properties of the epoxy matrix.

Table 2: Volume fraction of nanochannels, average fiber diameter, flexural strength (σ) and modulus (E) of the samples, and their reduction compared to the water immersed epoxy control (E-H_2O) which was pretreated in H_2O in the same way as the nanovascularized samples. Sample designation: C stands for channels, the following number indicates the volume percentage of nanochannels in the sample, and the last word indicates the size of the nanochannels.

Sample	Channels (vol %)	Diameter (nm)	σ (MPa)	Red (%)	E (GPa)	Red (%)
E-H_2O	0	-	104 ± 1	-	2.7 ± 0.1	-

C6-fine	6	390 ± 83	91 ± 6	12 ± 7	2.7 ± 0.1	1 ± 8
C6-coarse	6	760 ± 92	80 ± 5	23 ± 7	2.2 ± 0.1	19 ± 8
C9-fine	9	250 ± 65	72 ± 8	30 ± 9	2.4 ± 0.2	14 ± 10
C9-coarse	9	830 ± 130	64 ± 6	38 ± 7	1.8 ± 0.2	33 ± 10

Our results show that, although there is a loss of mechanical strength by introducing a nanovascular network in an epoxy, by introducing microcapsules there is a decrease reported as well [9,10,12]. Although a strict comparison would not be fair because the materials are different (e.g. matrix, filled microcapsules with a solid shell compared to an empty nanovascular network);for a 6 vol% nanovascular network, the decrease of the flexural strength of the nanovascularized epoxy is around 10 % for the fine nanochannels and 20 % for the larger nanochannels, in comparison with a circa 40 % reduction on introduction of filled microcapsules [9]. In addition, microsized reservoirs, including microcapsules, hollow glass fibers, and microvascular networks, have the extra inconvenience that they do not fit in the resin-rich interlayer of a fibre-reinforced composite. Therefore, they displace and distort the reinforcement architecture, which causes large loss of strength [13–15]. This problem can be overcome by the introduction of a nanoscale network, which will not deform the reinforcement architecture.

Another drawback of the proposed method is the slow dissolution of the pullulan nanofibers and the slow take up of the healing agents. Core-shell nanofibers could solve these problems and have even smaller loss of mechanical properties. In these core-shell nanofibers, a liquid healing agent can be embedded in the core, while the pullulan shell will maintain mechanical stability. Therefore, we can conclude that this technique has potential for creating a nanovascular network for self-healing polymers, but even more important for coaxial nanofibers which contain the healing agents as liquid cores.

5. CONCLUSIONS

In the context of the development of self-healing composites matrices using self-healing agents loaded in nanovascular networks, rather than in microcapsules, the effect of introducing a nanovascular network on the flexural properties of an epoxy resin was studied. Epoxy resins with nanovascular networks having volume fractions of nanochannels of 6 to 9 vol% and channel diameters ranging from 250 to 830 nm were prepared by selectively dissolving embedded networks of electrospun pullulan nanofibers. The desired morphology and diameter of nanofibers for the targeted nanovascular application can be created by tuning the concentration of the solution and the humidity at which it is electrospun.

As expected, the flexural strength decreases with the introduction of such a porous network. However, this decrease can be reduced by introducing smaller nanochannels. Further, the results show a major improvement compared with the introduction of filled microcapsules for the same amount of healing agent. Moreover, the absence of a reduction of the mechanical properties on embedding pullulan nanofibers in the epoxy matrix indicates an even higher potential for self-healing composites based on embedded networks of coaxial nanofibers that contain the liquid healing agents in their cores, eliminating the need for dissolving the sacrificial fibres and infusing healing agents in the nanovascular networks. This is very important for structural self-healing applications and will be studied in future work.

6. ACKNOWLEDGEMENTS

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Figure 1: Schematic drawing of the methodology, including the optimization of the electrospinning process, the fabrication of the nanocomposite and the nanovascular network, and the flexural testing on the nanocomposite and the nanovascular network.

Figure 2: The average fiber diameter increases linearly and the viscosity increases according to a power law as a function of the concentration of Pullulan in the aqueous solution for the range of concentrations tested. The trendlines, a linear one for the average fibre diameter and a power one for the viscosity, are fit to the data.

Figure 3: SEM images of pullulan nanofibers electrospun at 30, 50 and 70 % RH from aqueous solutions of 15, 25 and 35 wt% pullulan showing the difference in morphology and diameter of the nanofibers.

Figure 4: The average pullulan fiber diameter decreases with increasing humidity. The grey square indicates the process window where defect-free fibers can be electrospun.

Figure 5: SEM images of the different steps of fabrication of the nanovascular network: a) the pullulan nanofibers prior to their embedment in the epoxy matrix; b) cross section of the composite containing the sacrificial pullulan nanofibers after the curing of the epoxy matrix; and c) cross section of the nanovascular network of channels after the dissolution of the nanofibers by immersion in water. The square and the circle show the interconnections of the nanochannels.

Figure 6: Mass loss (wt%) of one specimen from each sample due to the dissolution of the pullulan nanofibers in water over time.